

From: Frank Rogenberg 1 (903) 376-8429

To: Yong Wang (509) 3765106

2-07-6, Sunday, January-28-2001 9:14pm

## PATENT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Wang et al.

Application No. 09/375,615

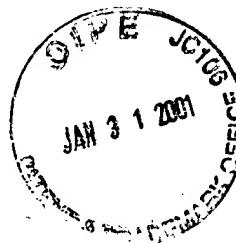
Art Unit: 1764

Filed: Aug 17, 1999

Examiner: B. Yildirim

For: A METHOD AND CATALYST  
STRUCTURE FOR STEAM  
REFORMING OF A  
HYDROCARBON

Atty Docket: B-1482

DECLARATION PURSUANT TO 37 C.F.R. § 1.132Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

1. I, Yong Wang, received a Ph.D. in Chemical Engineering from Washington State University in 1993. Since that time, I have been employed by the Battelle Memorial Institute in the Pacific Northwest National Laboratory in Richland, Washington. My current job title at Battelle is Chief Scientist.

2. All of the data described in this Declaration and accompanying attachments was collected at the Pacific Northwest National Laboratory. The data was obtained by myself and/or by my coworkers. I have personal knowledge of the conditions under which this data was acquired.

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3. The data set forth in Attachments 1-4 was collected over the powder catalyst described in the patent application. As stated in the application, this catalyst was prepared by ~~The-supported-catalyst-was-prepared-by~~ (1) calcining a high surface area  $\gamma$ - $\text{Al}_2\text{O}_3$  at 500 °C for 5 hours; (2) impregnating the  $\gamma$ - $\text{Al}_2\text{O}_3$  with MgO using the incipient wetness technique with a solution of magnesium nitrate; and obtaining an MgO-modified  $\gamma$ - $\text{Al}_2\text{O}_3$  support; (3) drying the modified support at 110 °C for 4 hours followed by (4) a second calcination at 900 °C for 2 hours; (5) impregnating the modified support with  $\text{Rh}_2\text{O}_3$  with the incipient wetness technique from a rhodium nitrate solution; (6) followed by a final drying 110 °C for 4 hours and (7) a final calcination at 500 °C for 3 hours to obtain a powder of the supported catalyst.

A microreactor was constructed of a quartz tube with 4mm ID and 6.35 mm OD. About 0.2 g of powder of supported catalyst was placed in the microreactor in a packed bed arrangement.

4. The Table entitled "Powder Catalyst ..." (Attachment 1) shows that the inventive method (that is, steam reforming at short residence times over a spinel-supported catalyst) enables steam reforming of a variety of hydrocarbons including methane, butane, iso-octane, synthetic crude, gasoline, diesel, and JP-8. Conversions of 60% or greater were observed in each case. Carbon monoxide selectivities were observed as follows (in %): methanol (90.69), methane (61.7), butane (11.2), iso-octane (39.9), synthetic crude (26.9), gasoline (20.7), diesel (35.9) and JP-8 (27.5).

5. The graph entitled "SR of Butane ..." (Attachment 2) shows that the inventive method enables steam reforming of butane at a steam-to-carbon ratio of 3 with high conversion of hydrocarbon throughout the temperature range of 600 to 900 °C.

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6. The graph entitled "Effects of Steam Ratio" (Attachment 3) shows that at a residence time of 6.35 msec, greater than 50% hydrocarbon conversion was obtained throughout the range of steam-to-carbon ratio of from 1 to 3. Higher steam-to-carbon ratios results in higher methane conversions and lower CO selectivity.

7. The graph subtitled "Life Testing . . ." (Attachment 4) shows excellent maintenance of methane steam reforming activity at a residence time of 6.35 msec and 900°C throughout the range of steam-to-carbon ratio of from 1 to 3.

8. The graph titled "Engineered Catalysts - Various Forms" (Attachment 5) shows that, utilizing the inventive method, methane conversions in excess of 50% are obtained over a variety of catalyst configurations, arrangements, and short residence times. The graph entitled "Engineered Catalysts - Various Forms: CO Selectivity" (Attachment 6) shows that, utilizing the inventive method, CO selectivities less than about 70% can be obtained over a variety of catalyst configurations, arrangements, and short residence times. From the graph of CO selectivities it can be seen that higher pressures yield a lower percentage of CO.

Porous DE101010, C50, and DC110 catalysts contained a catalyst of 13.8% Rh/6% MgO/Al<sub>2</sub>O<sub>3</sub> on a metal felt of FeCrAl alloy (the alloy was obtained from Technetics, Deland, Florida). 13.8wt%Rh6wt%MgO/Al<sub>2</sub>O<sub>3</sub> powdered catalyst was prepared by 1) calcining a high surface area gamma-alumina at 500°C for 5 hours; 2) impregnating the gamma alumina with MgO using the incipient-wetness method with an aqueous solution of magnesium nitrate; and obtaining an MgO modified gamma alumina support; 3) drying the modified support at 110°C for 4 hours followed by 4)

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a second calcination at 900 °C for 2 hours; 5) impregnating the modified support with Rh<sub>2</sub>O<sub>3</sub> with the incipient wetness method from a rhodium nitrate solution; 6) followed by a final drying at 110 °C for 4 hours and a 7) final calcinations at 500 °C for 3 hours to obtain a powder of the supported catalyst. The powdered catalyst was ball-milled overnight and slurry dip-coated on the FeCrAl felt until the desired loading is achieved. The coated catalyst was dried at 90 °C overnight and calcined at 350 °C for four hours. Prior to the catalyst evaluation, catalyst was reduced in 10%H<sub>2</sub>/N<sub>2</sub> (100cc(STP)/min) at 110 °C for four hours.

All experiments were conducted to demonstrate the present invention using a microchannel for methane steam reforming. The microchannel was placed within a tube furnace to provide the required endothermic reaction heat. DFI01010 consists of two single felts. Both felt catalysts have the identical dimensions (0.01" x 0.35" x 2"), and were evaluated in a single channel device (0.03" x 0.35" x 2" / 0.075 cm x 0.88 cm x 5.0 cm). Two felts with a gap of 0.01" were placed in the single channel device so that both felts were in close contact with the walls. The catalyst chamber volume is defined as the single channel volume (0.03" x 0.35" x 2" / 0.075 cm x 0.88 cm x 5.0 cm).

C50 catalyst was configured as follows. Felt with a thickness of 0.01" (0.025 cm) was crimped into a corrugated form, and is called a ruffle. Ruffles studied in this work have a fixed wave length of 0.117" (0.295 cm) and a fixed amplitude of 0.05" (0.127 cm). The dimensions of ruffle are 0.35" (0.88 cm) in width and 2" (8.0 cm) length. Reactants flow in the direction perpendicular to the waves. Single ruffle was snug-fitted into a single channel device (0.05" x 0.35" x 2"), which confines the catalyst chamber volume. DCII01 has a double ruffle configuration, which is designed by stacking two identical ruffles with a shim (0.01" x 0.35" x 2" / 0.025 cm x 0.88 cm x 5.0 cm) in between. Double ruffle was

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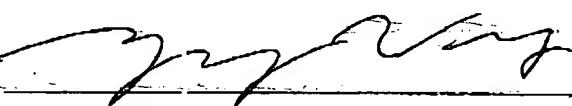
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evaluated in a wider single channel device (0.11" x 0.35" x 2" / 0.28 cm x 0.88 cm x 5.0 cm), which confines the catalyst chamber volume.

9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Signature



Yong Wang

Date

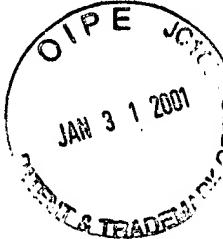
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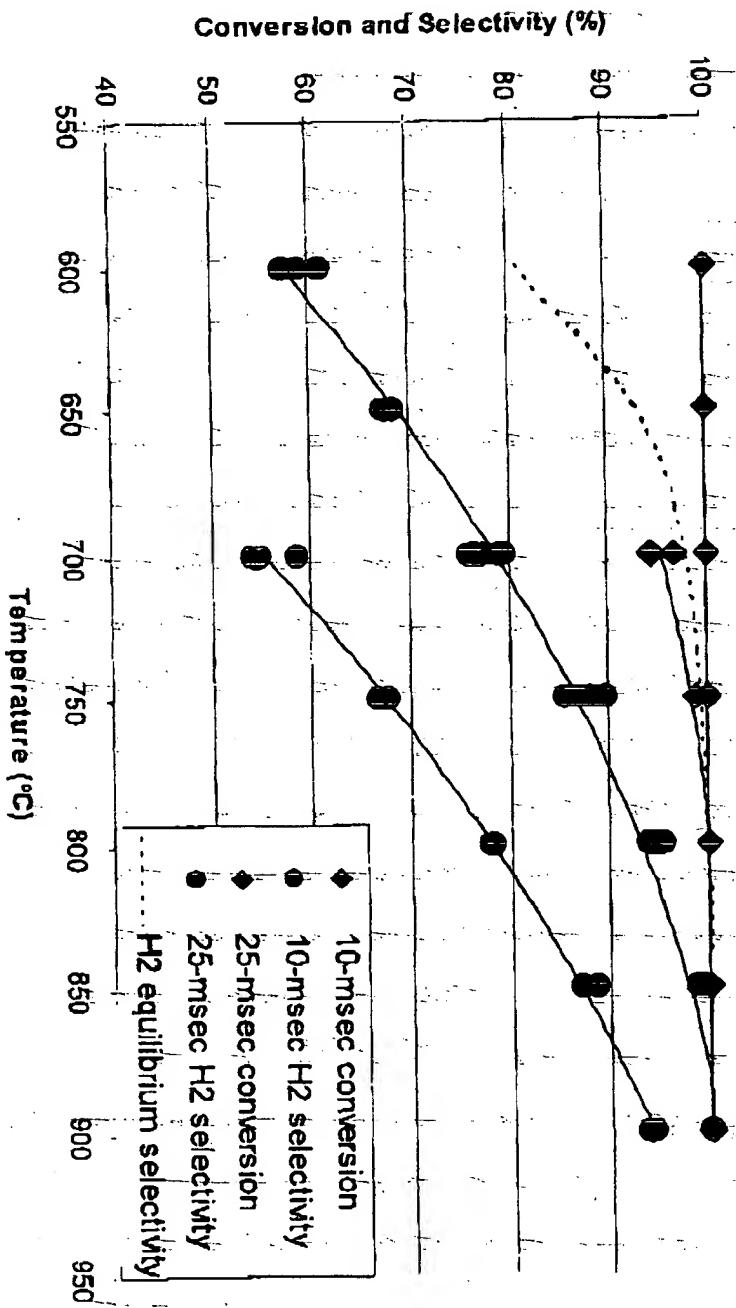
Attachment 1

Powder catalyst performance with B-14:H2 catalyst using various hydrocarbon fuels

HC	H2O/C	temp, C	P, atm	Tcont, s	Tres, s	Conv. %	S to H2%		S to CO%	H2 productivity, mmols/cc cat.
							S to H2%	S to CO%		
methanol	3	375	1	0.035	0.025	82.9	92.72	90.69		0.49
methane	3	631	1	0.025	0.011	99.58	100	61.7		1.33
butane	3	600	1	0.025	0.011	100	61	11.2		0.75
isooctane	3	650	1	0.025	0.011	100	87	39.9		1.06
syn crude	3	575	1	0.05	0.024	100.5	87.7	26.9		0.53
gasoline	3	650	1	0.025	0.011	60	100	20.7		0.73
diesel	3	650	1	0.025	0.011	93.2	99.8	35.9		1.12
JP-8	3	650	1	0.025	0.011	96	78	27.5		0.90

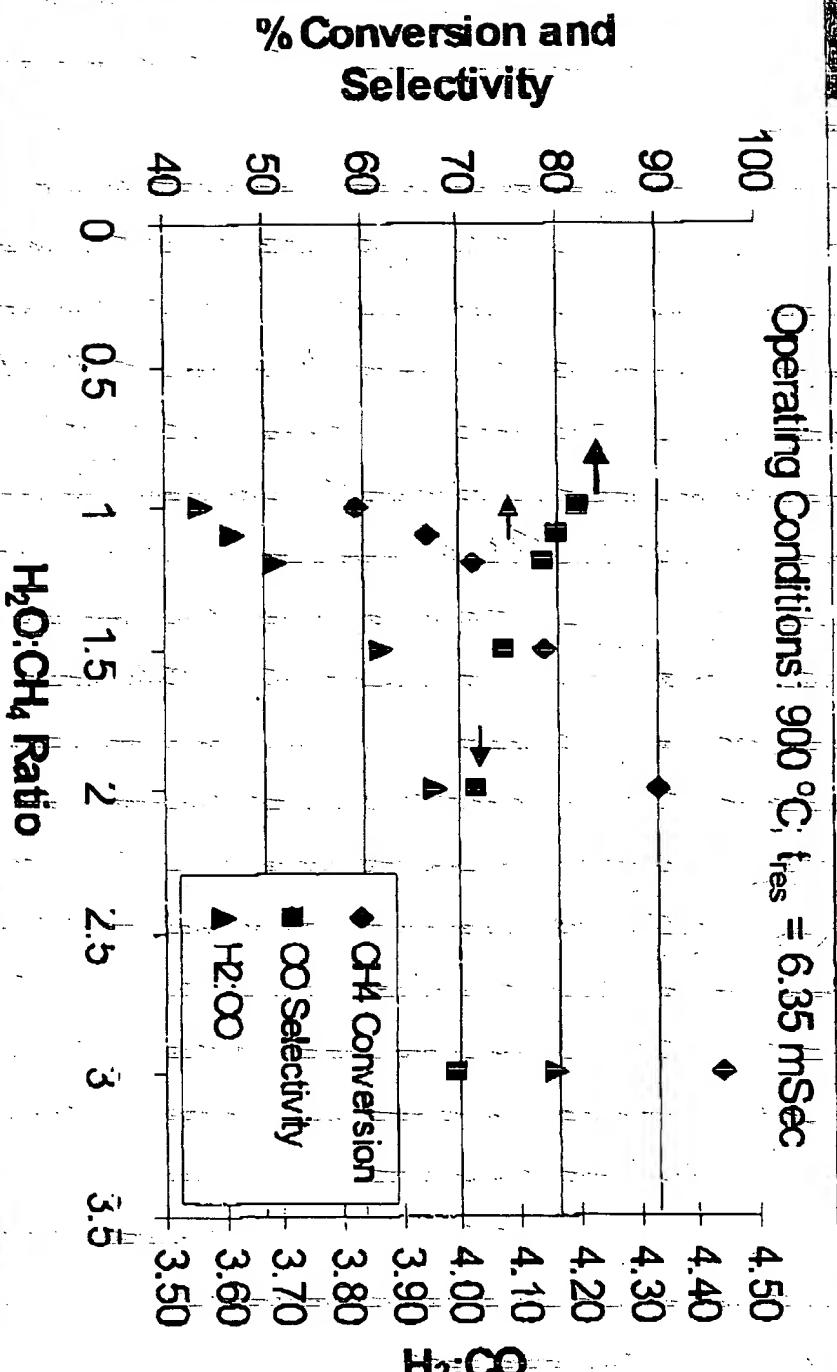
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# SR of Butane on Battelle Catalyst B (Powder, $H_2O/C=3$ , 1 atm)



Battelle

## Effects of Steam Ratio (Catalyst B)



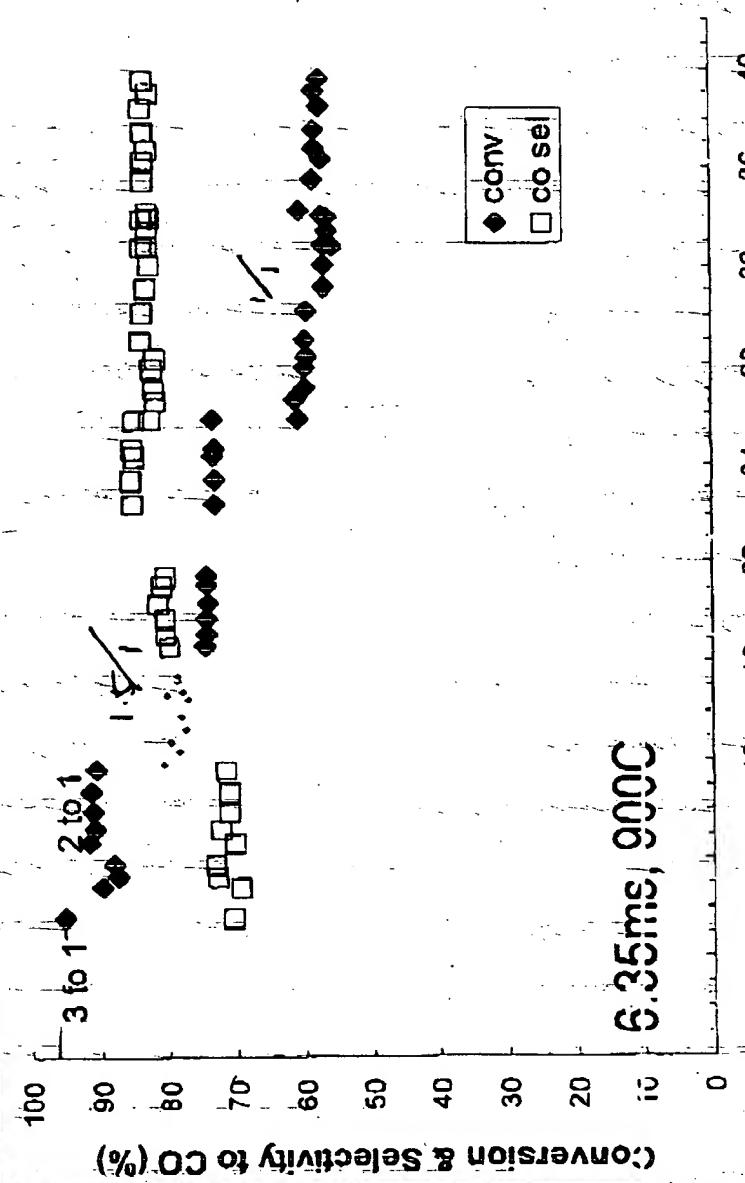
### Higher steam ratio:

- increases conversion and H<sub>2</sub>/CO ratio
- decreases CO selectivity

*Business Sensitive*

## 1st Development:

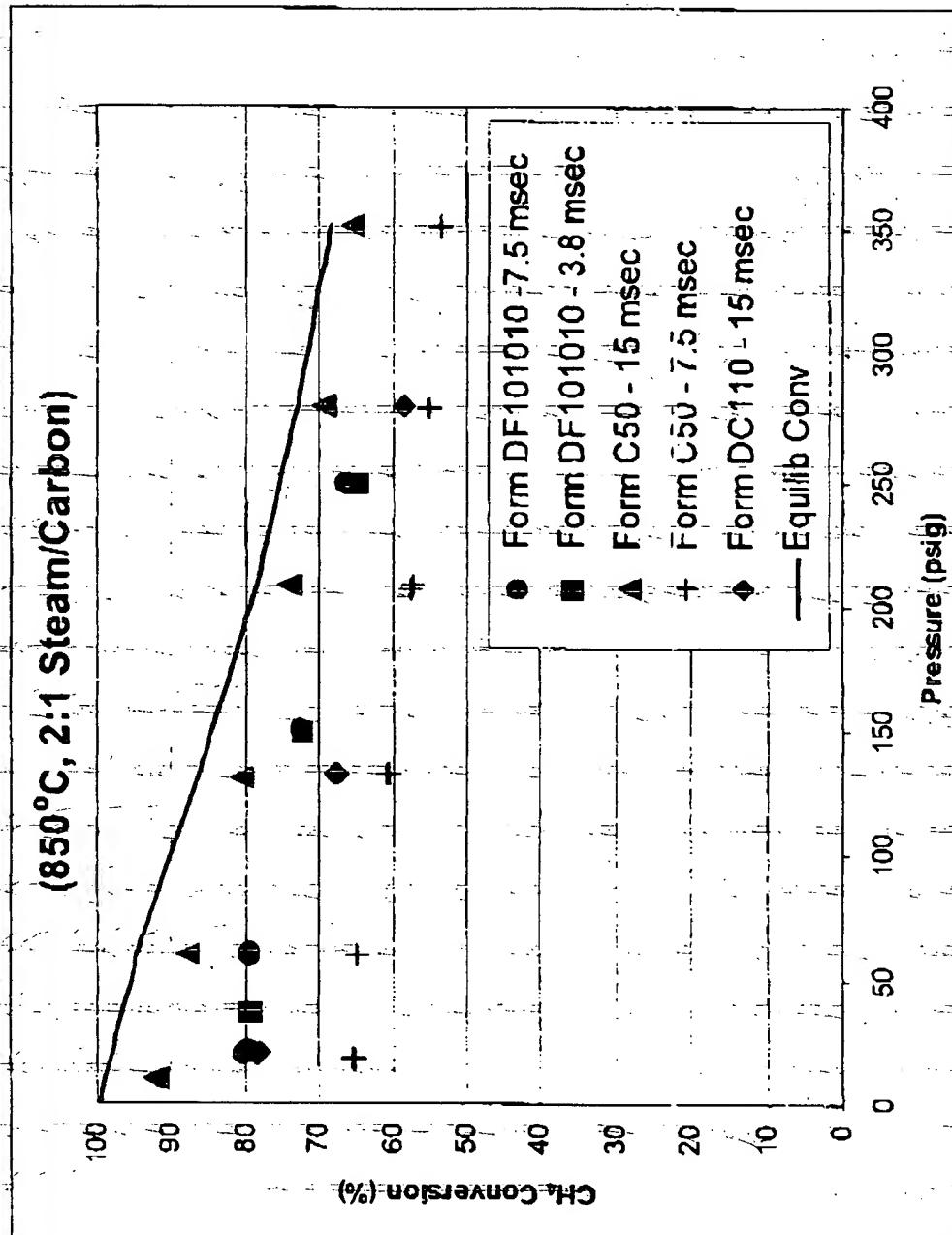
### Testing of Proprietary Catalyst for Methane SR as a Function of Steam ratio



Total Time on Stream (hrs)  
Conversion over the duration of experiments (42hours) with 9 thermal cycles

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# Engineered Catalysts – Various Forms



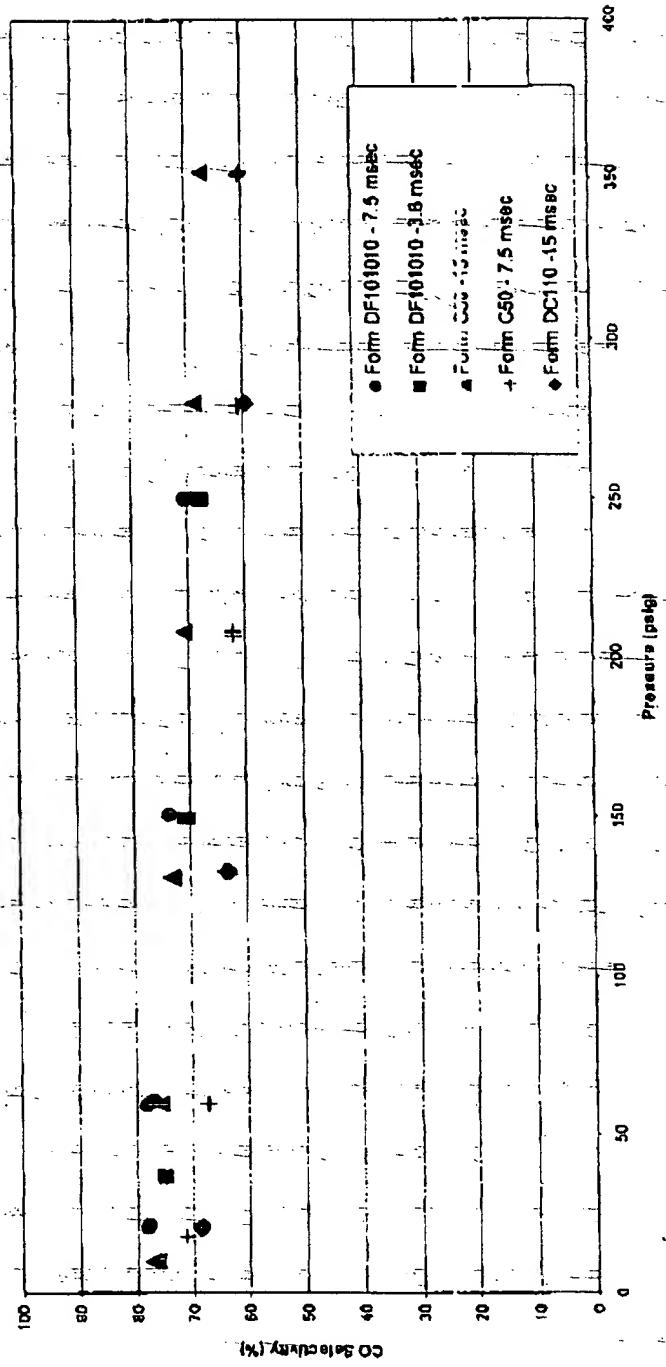
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# Engineered Catalysts – Various Forms:CO Selectivity (H<sub>2</sub> selectivity is 100%)

Engineered Catalyst Structures  
850C Constant Bed Temp: 2:1 Steam/Carbon



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